J. Am. Chem. Soc. **2001,** *123,* 763−764

Metal Sphere Photonic Crystals by Nanomolding

Lianbin Xu,[†,‡] Weilie Zhou,[‡] Mikhail E. Kozlov,[§,||]
Ilyas I. Khayrullin,[§,||] Igor Udod,[§] Anvar A. Zakhidov,[§]
Ray H. Baughman,*[,§] and John B. Wiley*[,†,‡]

Department of Chemistry and the
Advanced Materials Research Institute
University of New Orleans
New Orleans, Louisiana 70148-2820
Honeywell Int., Materials Laboratory
Morristown, New Jersey 07962-1021
New Jersey Institute of Technology
Newark, New Jersey 07102-1982

Received October 25, 2000

Crystals of nanosize metal spheres have potential applications as diverse as photonics, thermoelectrics, and magnetics.[1,2] Though methods exist for the chemical synthesis of metal nanospheres[3] and the self-assembly of these spheres into submicron thick crystals,[1] the fabrication of large crystals has been illusive. In contrast, centimeter-size face-centered-cubic (fcc) crystals of SiO_2 nanospheres (porous opals) can be routinely fabricated by sphere self-assembly.[4] Since no methods are available for growing large crystals of metal nanospheres, we have developed a different approach which builds upon recent success[5−12] in the fabrication of *inverse opals*. Since these inverse opals replicate the void space of ordinary porous SiO_2 opals (Figure 1a), we can use them as nanomolds for “casting” crystals of metal nanospheres. Herein we present two methods based on this strategy for the fabrication of large crystals of metal nanospheres, including NaCl-type crystals based on two different size nanospheres. This NaCl structure was previously obtainable only for metal sphere sizes an order of magnitude smaller than the photonic crystal range.[13]

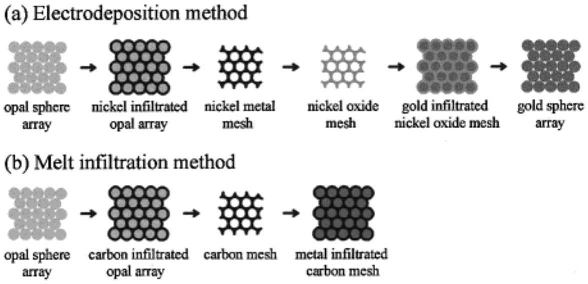

Figure 1. Sequential methods for the preparation of metal nanosphere arrays (a) in a nonconductive matrix and (b) in a conductive carbon matrix.

In the first method (Figure 1a), a sequence of electrochemical and chemical steps was used to prepare metal sphere arrays within a nonconductive matrix. Initially, an fcc porous opal slab containing 290 nm diameter spheres was electrochemically infiltrated[11] with nickel. After removal of the opal template with a 2% HF solution, the nickel mesh was slowly oxidized in air at 550 °C for 8 h (Figure 2a). The resulting poorly conducting nickel oxide mesh was then used as a nanomold for the electrochemical growth of a gold nanosphere array. Finally, the NiO template was removed in dilute sulfuric acid to produce an $\sim$30 μm thick array of gold nanospheres (Figure 2b,c).

In the second approach (Figure 1b), periodic nanosphere arrays were fabricated by the infiltration of molten metals into carbon inverse opals made by the phenolic process[6] (Figure 2d). This melt infiltration (at close to the melting point and pressures of 1−2 kbar) resulted in nanosphere crystals for elemental metals and semiconductors (Pb, Bi, Sb, and Te) and thermoelectric alloys (Bi−Sb, Bi−Te, and Bi−Te−Se). A typical SEM image of a fracture surface (Figure 2e) for centimeter dimension sample shows that the melt-infiltration results in a high-fidelity inverse replica of the carbon matrix, which is itself a high-fidelity inverse replica of the original SiO_2 opal. Since the minimum radius of the infiltrated material decreases with pressure, the applied pressure during solidification can be used to control the interconnections between spheres, and thereby the electrical and thermal transport properties of the sphere array. Moreover, the carbon of the inverse replicas either substantially fills the void space of the original SiO_2 opal or coats only the internal surfaces.[6] In this latter case, the void space in the carbon replica comprises two separate labyrinths (percolated spherical voids and a percolated network of octahedral and tetrahedral void spaces). SEM measurements (Figure 2f) show that both of these labyrinths can be filled by melt infiltration at kilobar pressure to make the nanosphere version of a NaCl-type structure.

Since these metal sphere arrays are metallodielectric photonic crystals, new properties should arise which are absent for dielectric photonic crystals—like the plasmon gap observed in the microwave or infrared[14,15] for metal meshes. These fabrication methods are applicable to various metals, semiconductors, and insulators,[16] and can be used to make nanocomposites. By melt infiltrating an antimony inverse opal (made by infiltrating antimony into a SiO_2 opal, and extracting the SiO_2) with bismuth, we obtained a

---

[*] To whom correspondence should be addressed. E-mail: jwiley@uno.edu and ray.baughman@honeywell.com.

[†] Department of Chemistry, University of New Orleans.

[‡] Advanced Materials Research Institute, University of New Orleans.

[§] Honeywell Int.

[||] New Jersey Institute of Technology.

(1) Sun, S.; Murray, C. B.; Weller, D.; Folks, L.; Moser, A. *Science* **2000**, *287*, 1989−1992.

(2) Moroz, A. *Phys. Rev. Lett.* **1999**, *83*, 5274−5277.

(3) Goia, D. V.; Matijevic, E. *New J. Chem.* **1998**, 1203−1215.

(4) Xia, Y.; Gates, B.; Yin, Y.; Lu, Y. *Adv. Mater.* **2000**, *12*, 693−713 and the references therein.

(5) Holland, B. T.; Blanford, C. F.; Stein, A. *Science* **1998**, *281*, 538−540.

(6) Zakhidov, A. A.; Baughman, R. H.; Iqbal, Z.; Cui, C.; Khayrullin, I.; Dantas, S. O.; Marti, J.; Ralchenko, V. G. *Science* **1998**, *282*, 897−901.

(7) Johnson, S. A.; Ollivier, P. J.; Mallouk, T. E. *Science* **1999**, *283*, 963−965.

(8) Velev, O. D.; Tessier, P. M.; Lenhoff, A. M.; Kaler, E. W. *Nature* **1999**, *401*, 548.

(9) Jiang, P.; Cizeron, J.; Bertone, J. F.; Colvin, V. L. *J. Am. Chem. Soc.* **1999**, *121*, 7957−7958.

(10) Braun, P. V.; Wiltzius, P. *Nature* **1999**, *402*, 603−604.

(11) Xu, L.; Zhou, W. L.; Frommen, C.; Baughman, R. H.; Zakhidov, A. A.; Malkinski, L.; Wang, J.-Q.; Wiley, J. B. *Chem. Commun.* **2000**, 997−998.

(12) Blanco, A.; Chomski, E.; Crabtchak, S.; Ibisate, M.; John, S.; Leonard, S. W.; Lopez, C.; Meseguer, F.; Miguez, H.; Mondia, J. P.; Ozin, G. A.; Toader, O.; van Driel, H. M. *Nature* **2000**, *405*, 437−439.

(13) Kiely, C. J.; Fink, J.; Zheng, J. G.; Brust, M.; Bethell, D.; Schffrin, D. J. *Adv. Mater.* **2000**, *12*, 640−643.

(14) Sievenpiper, D. F.; Stickmiller, M. E.; Yablonovitch, E. *Phys. Rev. Lett.* **1996**, *76*, 2480−2483.

(15) Zakhidov, A. A.; Baughman, R. H.; Khayrullin, I. I.; Udod, I.; Kozlov, M.; Eradat, N.; Vardeny, V. Z.; Sigalas, M.; Biswas, R. *Synth. Met.* **2001,** *116*, 419−426.

10.1021/ja005733y CCC: $20.00

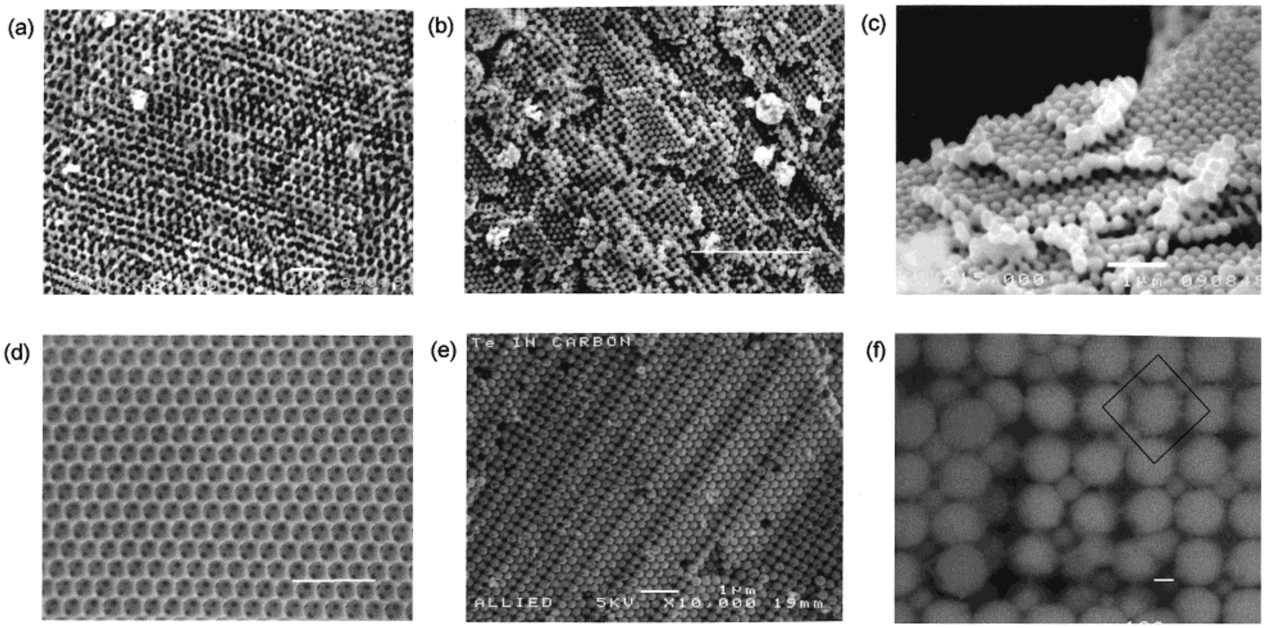

Figure 2. (a) SEM of nickel oxide template used in electrochemical nanomolding, (d) fracture-surface image of a fcc phenolic inverse opal, which in the carbonized state is used as a template for nanomolding by the melt process, (b, c, e, f) fracture-surface SEM images of fcc sphere arrays made by replicating the void space of a porous SiO_2 opal and then replicating the void space of the resulting replica. In panels b and c, arrays of gold spheres were made using two electrochemical replication processes. In panels e and f, sphere arrays were made by replicating the void space of a carbon inverse opal by melt infiltration of tellurium (e) and bismuth (f). In panel f, large metal spheres occupy the corners of the unit cell face (indicated by the square) and smaller metal spheres occupy (or fractionally occupy) the sites between the large spheres, as in the NaCl structure. Stacking faults on close-packed planes in the original SiO_2 opal are replicated in the fabricated sphere arrays, bringing (100) and (111) planes into near coincidence in panels b and e. The length scales are 1 μm except for panels b and f, which are 5 μm and 100 nm, respectively.

thermoelectric "hyper alloy" in which a fcc array of Bi spheres are in an antimony matrix. By applying similar methods to optimally selected thermoelectrics and to combinations of hard and soft ferromagnets, it may be possible to engineer high-efficiency thermoelectrics and magnets with high-energy storage capabilities.

Acknowledgment. Work supported by the Department of Defense (DARPA MDA972-97-1-0003 and DAAB07-97-C-J036).

JA005733Y

---

(16) Note Added in Proof: (a) In November 2000, a similar approach was used for the preparation of ordered hollow titania spheres, see: Rengarajan, R.; Jiang, P.; Colvin, V.; Mittleman, D. *Appl. Phys. Lett.* **2000**, *77*, 3517−3519. (b) Analogous electrochemical strategies have been used for the preparation of one-dimensional porous membranes, see: Hoyer, P.; Masuda, H. J. *Mater. Sci. Lett.* **1996**, *15*, 1228−1230.